

# TRANSLATION



[11] Publication number:  
0,083,933  
A1

[12] EUROPEAN PATENT APPLICATION

[21] Application number: 83,100,078.1

[51] Int. Cl.3: C 09 K 5/04

[22] Date of filing: January 7, 1983

[30] Priority:  
January 13, 1982  
DE 32 00 736 (Germany)

[43] Date of publication of application:  
July 20, 1983 Bulletin 83/29

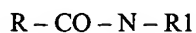
[84] Designated Contracting States:  
DE, FR, IT, NL, SE

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[54] Working medium for sorption heat pumps.

EP [57] Sorption heat pumps can make use of working media that consist of a fluorinated hydrocarbon or  
0,0 fluorochlorinated hydrocarbon containing hydrogen and of a liquid compound having the formula  
83,  
93  
3  
A1



R2

wherein

R2 stands for a C1 to C4-alkyl radical,

R1 stands for a C1 to C10-alkyl radical or acetyl radical, and

R stands for a hydrogen atom or for a C1-C10-alkyl radical,

or else

R and R2 together stand for an alkylene group or alkenylene group having together 3 to 5 carbon bridge members that can also be substituted by methyl groups, with the proviso that R, R1 and R2 together contain between 4 and 15 carbon atoms.

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### Working medium for sorption heat pumps

The present invention relates to a working medium which contains a fluorinated hydrocarbon or fluorochlorinated hydrocarbon containing hydrogen and which can be employed in heat pumps of the absorption type for purposes of generating heat or cold.

The use of heat pumps for heating or cooling purposes has long been known. Whereas in the beginning electrically powered compression machines were in the foreground for refrigeration applications, heat pumps for heating purposes that are capable of saving energy have aroused interest recently. In this context, compression heat pumps as well as sorption heat pumps can be used in principle. Sorption heat pumps, however, have a number of advantages over electrically powered compression heat pumps, primarily the low level of noise, less wear since there are hardly any mechanically driven parts, fewer maintenance requirements, lower equipment costs and especially lower consumption of primary energy. With an electrically powered compression heat pump, it is necessary to take into account, for example, that, by the time the electricity is available for use, about two-thirds of the primary energy has been lost.

Substance pairs for sorption heat pumps consisting of a solvent and a volatile substance that is going to be dissolved are already known. Such substance pairs were first developed for use in industrial refrigeration equipment (water/ammonia; lithium bromide + water/water). For private households, however, the use of ammonia is limited due to toxicological and safety considerations. Combinations with lithium bromide make high requirements in terms of the sealing conditions since the installations operate under a high vacuum.

When it comes to use in smaller systems, especially in private households, systems have been proposed that contain a fluorochlorinated hydrocarbon as the volatile phase, since this substance group is not flammable, relatively non-toxic and non-corrosive.

Substance pairs for sorption heat pumps in which the solvent is a phosphoric acid amide having alkyl or phenyl groups and the volatile phase is a fluorochloroalkane are the subject matter of German Preliminary Published Application No. 29 44 189.

The currently most suitable system of a fluorochlorinated hydrocarbon with a solvent is considered in the technical literature to be the combination of HFC 22 (monochlorodifluoromethane) with tetraethylene

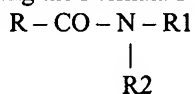
glycoldimethyl ether (B. Eisemann, "Absorption refrigeration", in ASHRAE Journal, December 1959, pages 45 to 50; S. Mastrangelo, "Chlorofluorohydrocarbons in tetraethylene glycoldimethyl ether", in ASHRAE Journal, October 1959, pages 64 to 67; K. Stephan, D. Seher, "Arbeitsgemische für Sorptions-Wärmepumpen" [Operating mixtures for sorption heat pumps] in Klima-Kälte-Heizung [Air-conditioning-Refrigeration-Heating] 1/1980, pages 874 and 875).

A substance pair (consisting of the working substance and the solvent) is suitable for use in sorption heat pumps, especially if the degassing range of the working substance is large, since this allows the transportation of a large volume of heat per unit of weight of the solvent. The term degassing range refers to the difference between the solubility of the working substance in the absorber and the solubility of the working substance in the generator, expressed in kilograms per kilogram of solvent. The reciprocal value of this measured quantity indicates the amount of solvent to be pumped over per kilogram of the working substance. For the known system consisting of HFC 22 and tetraethylene glycoldimethyl ether, the degassing range is 0.19 kg/kg of solvent at 5 bar and at a solubility temperature of 50°C [122°F] in the absorber and at 10 bar and 130°C [266°F] in the generator. This means that 5.3 kg of solvent have to be pumped over per kilogram of HFC 22. For the same system, the sorption enthalpy of HFC 22 at 50°C [122°F] is – 310 kJ/kg of HFC 22. This quantity includes the evaporation enthalpy of HFC in the amount of 154 kJ/kg.

It is likewise advantageous for the solvent to have a specific heat and a viscosity that are as low as possible. Values of 2.16 kJ/kg K and 2.04 mm<sup>2</sup>/s have been found for tetraethylene glycoldimethyl ether.

The invention is based on the objective of creating a pair of working substances that transport a considerable higher quantity of heat per unit of weight of solvent but that likewise fulfill the other requirements made of such a system. In other words, for example, the system should not be corrosive. It should be possible to use it to withdraw heat from the surroundings at – 20°C [– 4°F]. At temperatures ranging from 150°C to 250°C [302°F to 482°F], it should be possible to expel the working substance from the solvent.

A working medium has now been found that achieves this objective and that contains another solvent in addition to a fluorinated hydrocarbon or fluorochlorinated hydrocarbon containing hydrogen. This solvent consists of at least one liquid acid amide having the Formula I below



wherein

R2 stands for C1 to C4-alkyl,

R1 stands for C1 to C10-alkyl or for acetyl, and

R stands for C1-C10-alkyl or for hydrogen,

or else

R and R2 together stand for an alkylene group or alkenylene group having together 3 to 5 carbon bridge members that can also be substituted by methyl groups, with the proviso that R, R1 and R2 together contain between 4 and 15 carbon atoms.

The alkyl radicals R, R1 and R2 can be linear or branched or can stand for cycloalkyl radicals such as, for instance, the cyclohexyl radical. Preference is given to alkyl radicals C1-C6, especially C1-C4. Examples of alkenyl groups having 3 to 5 carbon bridge members are the groups  $-(CH_2)_3-$ ,  $-(CH_2)_4-$ ,  $-(CH_2)_5-$ ,  $-(CH_2)_2-CH_3-CH-$ ,  $-(CH_2)_2-CHCH_3-CH_2-$ ,  $-(CH_2)_3-CHX$  wherein  $X = CH_3$  or  $C_2H_5$ . Preference is given to liquid acid amides having a boiling point above  $160^\circ C$  [ $320^\circ F$ ], especially above  $180^\circ C$  [ $356^\circ F$ ]. Among the non-cyclical acid amides, preference is given to compounds in which R1 and R2 are identical. A number of acid amides that can be employed according to the invention are given as examples in Tables 1 and 2.

Examples of suitable fluorine compounds containing hydrogen are the compounds  $CH_2F_2$ ,  $CF_3CH_3$ ,  $C_2HClF_4$  and especially  $CF_2ClH$  (HFC 22) as well as  $C_3F_7H$  (HFC 227). The fluorine compound should have a boiling point below  $0^\circ C$  [ $32^\circ F$ ]. Preference is given to fluorochlorinated compounds having 1 to 3 carbon atoms.

The degassing range of the new systems is markedly larger than with the system consisting of HFC 22 and tetraethylene glycoldimethyl ether. This is why the quantity of heat that can be transported per kilogram of solvent is considerably larger with the working media according to the invention. The sorption heat pumps filled with the substance pairs according to the invention can be operated as a refrigerating machine as well as a heat pump for heating purposes. The use of substance pairs according to the invention in a heat pump for heating purposes offers energy-related advantages when compared to their use in compression heat pumps. In the case of operation as a refrigeration machine, the advantages in comparison to a compression refrigeration installation (more favorable energy consumption) come to the fore primarily in larger installations.

The use of the invention in a sorption heat pump will be described in greater detail below using a working medium consisting of HFC 22 and 1-methyl-2-pyrrolidone (MPY) and illustrated with reference to the

figure. Under the above-mentioned conditions, this system exhibits a degassing range of 0.23 kg/kg of solvent; in other words, 4.3 kg of solvent are to be pumped over per kilogram of HFC. The sorption enthalpy amounts to  $-280$  kJ/kg, the viscosity at  $50^{\circ}\text{C}$  [ $122^{\circ}\text{F}$ ] is  $1.18$  mm<sup>2</sup>/s and the specific thermal capacity at  $50^{\circ}\text{C}$  [ $122^{\circ}\text{F}$ ] is  $1.9$  kJ/kg K.

The solution consisting of HFC 22 in MPY is heated up in the generator 1, during which process the HFC 22 is expelled. HFC 22 having only small fractions of MPY flows in gaseous form at an unchanged pressure through line 2 and reaches condenser 3. The temperature used in 1 leads to such a high vapor tension of HFC 22 that the HFC 22 can condense at the desired operating temperature of the condenser 3. The heat of condensation is released at the melting point (approximately  $50^{\circ}\text{C}$  [ $122^{\circ}\text{F}$ ], depending on the pressure) and can likewise be transferred to the object to be heated. The liquid HFC 22 is expanded via line 4 and throttle valve 5 at a low pressure in the evaporator 6, picking up heat from the surroundings at a low temperature. The vaporous HFC 22 passes through line 7 to reach the absorber 8, where the HFC 22 is dissolved in the solution of MPY, which has been depleted of HFC 22 and which was fed in from generator 1 via line 9, thereby transferring heat to the object to be heated. The solution of MPY, which has been enriched with HFC 22, leaves the absorber 8 and is pumped back to generator 1 by means of pump 12 via lines 10 and 11. On its way through the heat exchanger 13, the diluted solution from line 9 transfers heat to the enriched solution in line 10. If hydrogen or another inert gas is additionally present in the system, the mechanical pump 12 can be replaced with a vapor-bubble pump.

The evaporation of the liquid HFC 22 downstream from 5 into 6 can give rise to temperatures within the range from  $-20^{\circ}\text{C}$  to  $+40^{\circ}\text{C}$  [ $-4^{\circ}\text{F}$  to  $+104^{\circ}\text{F}$ ], preferably from  $-10^{\circ}\text{C}$  to  $+20^{\circ}\text{C}$  [ $+14^{\circ}\text{F}$  to  $+68^{\circ}\text{F}$ ], especially from  $-5^{\circ}\text{C}$  to  $+10^{\circ}\text{C}$  [ $+23^{\circ}\text{F}$  to  $+50^{\circ}\text{F}$ ]. For instance, the heat from the surroundings at a temperature of  $0^{\circ}\text{C}$  [ $32^{\circ}\text{F}$ ] and a pressure of 5 bar in the evaporator can be picked up. In this case, the depleted solution still contains about 0.65 kg of HFC 22 per kilogram of solvent. At the same pressure but at a higher temperature, the vapor of the HFC 22 is absorbed in the absorber 8. The absorption can take place at temperatures between  $20^{\circ}\text{C}$  and  $80^{\circ}\text{C}$  [ $68^{\circ}\text{F}$  and  $176^{\circ}\text{F}$ ], preferably between  $35^{\circ}\text{C}$  and  $65^{\circ}\text{C}$  [ $95^{\circ}\text{F}$  and  $149^{\circ}\text{F}$ ]. A solution of MPY containing only a small amount of HFC 22 and stemming from generator 1 serves as the absorption agent. In this process, the load rises to 0.88 kg of HFC 22 per kilogram of MPY. The fortified solution is conveyed at the same temperature to the generator 1, where the rich solution is heated by an external source of heat. This can be done at temperatures between  $90^{\circ}\text{C}$  and  $180^{\circ}\text{C}$  [ $194^{\circ}\text{F}$  and  $356^{\circ}\text{F}$ ], preferably between  $110^{\circ}\text{C}$  and  $150^{\circ}\text{C}$  [ $230^{\circ}\text{F}$  and  $302^{\circ}\text{F}$ ]. For example, the expulsion can take place at  $130^{\circ}\text{C}$  [ $266^{\circ}\text{F}$ ]. The heat flow into and out of the system is designated in the figure with the letter Q and its direction is indicated by the arrow. The position of the mid-points of the reactors 1 (generator), 3

(condenser), 6 (evaporator) and 8 (absorber) concurrently shows the pressure and temperature conditions prevailing in these reactors.

Another working medium on the basis of MPY having a favorable solubility range is the system made up of MPY/C3HF7. At 50°C [122°F] and 2.2 bar, 1.14 kg of MPY dissolve per kilogram of solvent (absorber); at 130°C [266°F] and 8.9 bar, only 0.48 kg of MPY dissolve per kilogram of solvent (generator), so that a degassing range of 0.66 kg/kg of solvent is achieved. Therefore, 1.52 kg of solvent have to be pumped over per kg of HFC.

It is surprising that the working media according to the invention, which are made up of special fluorochlorinated hydrocarbons and carboxylic acid amides, exhibit a larger degassing range than the system consisting of HFC 22 and tetraethylene glycoldimethyl ether.

The lower the temperature in the absorber, the higher the achieved load of acid amide with fluorinated hydrocarbon or fluorochlorinated hydrocarbon. The higher the temperature in the absorber, the lower the residual load. Therefore, the mixing ratio of acid amide to fluorine compound depends on the working conditions. In most cases, the fraction by weight of acid amide ranges from 10% to 75%, preferably 20% to 40%.

Table 1 – Non-cyclical amides having Formula I.

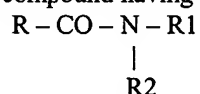
R	R1	R2
C3H7	C2H5	C2H5
C5H11	C2H5	C2H5
C7H5	C2H5	C2H5
C8H17	C2H5	C2H5
H	C3H7	C3H7
H	C4H9	C4H9
H	C5H11	C5H11
CH3	C3H7	C3H7
C4H9	C5H11	C5H11
CH3	COCH3	-H
C2H5	COCH3	-H

Table 2 – Cyclical amides having Formula I.

R1	R + R2
CH3	-(CH2)3-
C4H9	-(CH2)3-
CH3	-(CH2)2-CH-CH3-
CH3	-(CH2)2-CH-CH3-CH2-
CH3	-(CH2)3-CH-C2H5-
CH3	-CH=CH-CH=CH-
C2H5	-CH=CH-CH=CH-
CH3	(CH2)5

Patent Claims

1. A working medium for use in sorption heat pumps, consisting of a fluorinated hydrocarbon or fluorochlorinated hydrocarbon containing hydrogen and of a solvent, characterized in that the solvent consists of at least one liquid compound having the formula



wherein

R2 stands for a C1 to C4-alkyl radical,

R1 stands for a C1 to C10-alkyl radical or acetyl radical, and

R stands for a hydrogen atom or for a C1-C10-alkyl radical,

or else

R and R2 together stand for an alkylene group or alkenylene group having together 3 to 5 carbon bridge members that can also be substituted by methyl groups,

with the proviso that R, R1 and R2 together contain between 4 and 15 carbon atoms.

2. The use of the substance pair according to Claim 1 in a sorption heat pump.

Translation: Language Services Unit  
Leonardo and Elise Duvekot  
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February 24, 2003



European  
Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number:  
EP 83,100,078

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.3)
P, X	EP-A 0,062,516 (MATSUSHITA) * Claims 1, 2, 5 *	1,2	C 09 K 5/04
X	EP-A 0,030,127 (DAIKIN) * Claims 1, 4; Page 5, lines 20 through 25 *	1,2	
A	CHEMICAL ABSTRACTS, volume 95, 1981, page 149, no. 171820h, Columbus, Ohio, U.S.A. & JP-A 81 10953 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) March 11 1981, * Abstract *	1,2	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.3)
			C 09 K 5/00 F 25 B 29/00
Place of search: The Hague, The Netherlands		Date of completion of the search: April 20, 1983	Examiner: Nicolas H.J.F.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ..... &: member of the same patent family, corresponding document			